

PATENT APPLICATION
Docket No.: NC 84,337

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the application of: Feldstein
Serial No.: 09/917,649
Filed: 07/31/2001
For: FLUIDICS SYSTEM
Examiner: Ludlow, Jan M.
Art Group Unit: 1743

Honorable Commissioner of Patents
PO Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. § 1.131 OF ARTHUR W. SNOW

Sir:

I, Arthur W. Snow, hereby declare that:

1. I am a joint inventor of the invention claimed in the above-identified patent application.
2. Attached is a copy of portions of my invention disclosure, which formed the basis of this patent application.
3. The page titled "Patent Disclosure" bears a disclosure date of 05/15/1997. The contents of the disclosure were complete as of that date.
4. All work described in the disclosure was performed by me, my co-inventor, or under our supervision, no later than 05/15/1997 in NAFTA or WTO member countries.
5. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

18 Dec 2005

Date



Arthur W. Snow

Arthur W. Snow

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DECLARATION UNDER 37 C.F.R. § 1.131 OF HENRY WOHLTJEN

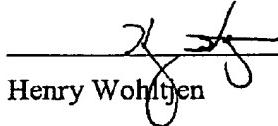
Sir:

I, Henry Wohltjen, hereby declare that:

1. I am a joint inventor of the invention claimed in the above-identified patent application.
2. Attached is a copy of portions of my invention disclosure, which formed the basis of this patent application.
3. The page titled "Patent Disclosure" bears a disclosure date of 05/15/1997. The contents of the disclosure were complete as of that date.
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16 Dec 2005

Date


Henry Wohltjen

PATENT DISCLOSURE

DISCLOSURE DATE: 15 May 1997

FIRST PUBLIC DISCLOSURE: None

INVENTION TITLE: CHEMICAL SENSOR

INVENTOR: Arthur W. Snow
& Hank Wohltjen

ASSIGNEE: Microsensor Systems, Inc.
62 Corporate Court
Bowling Green, KY 42103
(502) 745-0099

and

U.S. Naval Research Lab
Washington, DC

RELEVANT PATENTS: None known...
No search conducted

RELEVANT PUBLICATIONS: Schon & Simon
Snow & Wohltjen (to ^{be} submitted)

GENERAL PURPOSE OF THE INVENTION:

The purpose of this invention is to provide a simple, inexpensive method and apparatus for electronically sensing and monitoring the presence of chemical species.

WITNESSED AND UNDERSTOOD: C. Fletcher DATE: 6/11/97

WITNESSED AND UNDERSTOOD: William R. Bezugli DATE: 6/14/97

BACKGROUND:

The detection and monitoring of chemical species is important to many endeavors such as environmental monitoring and process control. This invention provides a simple method and apparatus by which the presence of chemical species can be electronically gauged.

The invention described here is especially well suited for applications that demand very compact size, low cost, and low power consumption. The method involves the measurement of the electrical resistance of a thin film of an electrically conductive material. Chemical vapors and liquids that come in contact with the thin film produce alterations in its electrical conductivity that are easily recorded.

The novel aspect of the approach disclosed here is the nature of the electrically conductive thin film that serves as the transduction medium. We use an extremely small cluster of gold atoms that forms a metallic "core" surrounded by a thin "ligand shell" of relatively non-conductive organic material that is covalently bound to the core through a thiol linkage. These types of material are well known in classical "gold sol" colloid chemistry. Precise control of the gold core size and the ligand shell thickness is afforded by the gold sol synthetic procedure and this precise control is a very important feature of this approach.

A chemical transducer is made when a large ensemble of these colloidal particles are deposited onto a surface equipped with a pair of electrical contacts. The resulting "device" can be described as a series of Metal-Insulator-Metal (MIM) junctions, where the metal is the gold core and the insulator is the ligand shell. For this reason we refer to the invention as a "Colloidal Metal-Insulator-Metal Ensemble" (or MIME device). By careful selection of an appropriate core size and ligand shell thickness, a wide range of film conductivities can be produced. Variations in the core size and ligand shell thickness also produce significant changes in the apparent sensitivity to chemical species exhibited by the device. Variations on the the chemical composition of the ligand shell produce significant changes in the chemical selectivity of the device.

WITNESSED AND UNDERSTOOD: R Shekhar DATE: 6/11/97

WITNESSED AND UNDERSTOOD: William R. Bangs Jr DATE: 6/12/97

The detailed mechanism of electronic charge transport through this device is not completely understood. It is known that the extremely small thickness of the insulating layer makes it highly probable that electronic tunneling occurs between the metal cores. It is also highly probable that electron hopping occurs across the atoms of the ligand shell material. It is well known that electron tunneling is extremely sensitive to the tunneling distance and the electron hopping is strongly affected by the electronic charge environment in the hopping path. Thus significant perturbations in the electrical conductivity of this material is predicted if the swelling of the film occurs due to the absorption of (e.g.,) chemical vapors (causing an increase in the apparent tunneling distance), or if the sorbate causes a small change in the electronic charge distribution in the ligand shell (thereby producing changes in the hopping current).

of
The colloidal size *if* the metal core-ligand shell causes the material to exhibit quantum properties that result from the extremely small size of the colloidal particle. Thus, the mechanism of operation of this sensing device is unlike any other well-known chemical sensor.

Another important feature of this system is that the ligand stabilized colloidal gold particles are essentially spherical in shape. Close packing of a large ensemble of these particles results in a material that contains substantial void spaces of a size that permits the rapid transport and diffusion of other chemical species throughout the ensemble (figure 1.).

WITNESSED AND UNDERSTOOD: R. Keehan DATE: 6/11/97

WITNESSED AND UNDERSTOOD: William R. Baugh Jr. DATE: 6/12/97

METAL-INSULATOR-METAL ENSEMBLE HYPOTHETICAL STRUCTURE

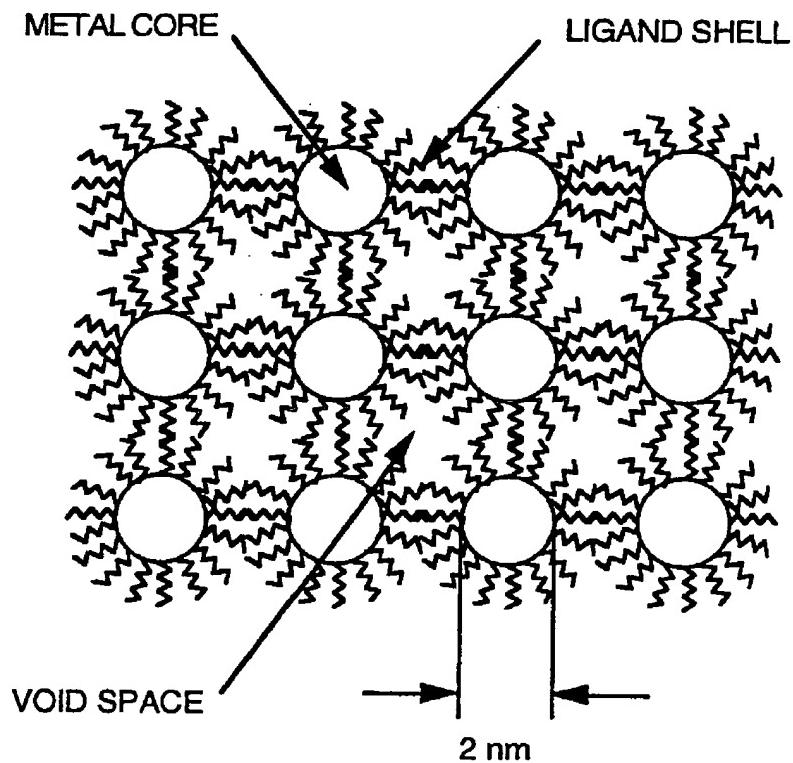


FIGURE 1.

WITNESSED AND UNDERSTOOD: D. Sheehan DATE: 6/11/97

WITNESSED AND UNDERSTOOD: William R. Baumgat DATE: 6/12/97

DESCRIPTION AND OPERATION OF THE INVENTION:

In its simplest form the invention consists of a pair of electrodes connected by a thin film of the colloidal metal-insulator-metal ensemble material (Figure 2.). A circuit is used to measure the electrical conductivity of the MIME device. The conductivity can be measured under AC or DC conditions.

While an apparatus as simple as this can be used, a preferred embodiment would use a pair of lithographically patterned (e.g., via photolithography, silk-screening, etc.) devices. The pattern would result in a planar interdigital "comb" electrode having a large ratio of electrode perimeter to electrode spacing. The large length-to-cross-sectional-area ratio serves to decrease the electrical resistance of the device, thereby making it very easy to measure the resistance variation with low noise and high precision. The preferred embodiment would also use a matched pair of these interdigital devices fabricated simultaneously on the same substrate (figure 3.). One device (the "sensor") would be exposed to the environment containing chemicals to be measured (gas, liquid, or solid), the other device (the "reference") would be covered with a passivating layer (e.g., plastic, glass, paraffin wax, etc.) or in some way isolated from the environment containing the chemical species to be measured. The reference device would provide a means to compensate the normal change in resistance with temperature exhibited by the MIME thin film. By fabricating the sensor and reference devices simultaneously, one is assured of accurate matching and highly reproducible system performance even if the lot-to-lot production process varies substantially.

WITNESSED AND UNDERSTOOD: C. D. Precain DATE: 6/11/97
WITNESSED AND UNDERSTOOD: William R. Bayly DATE: 6/12/97

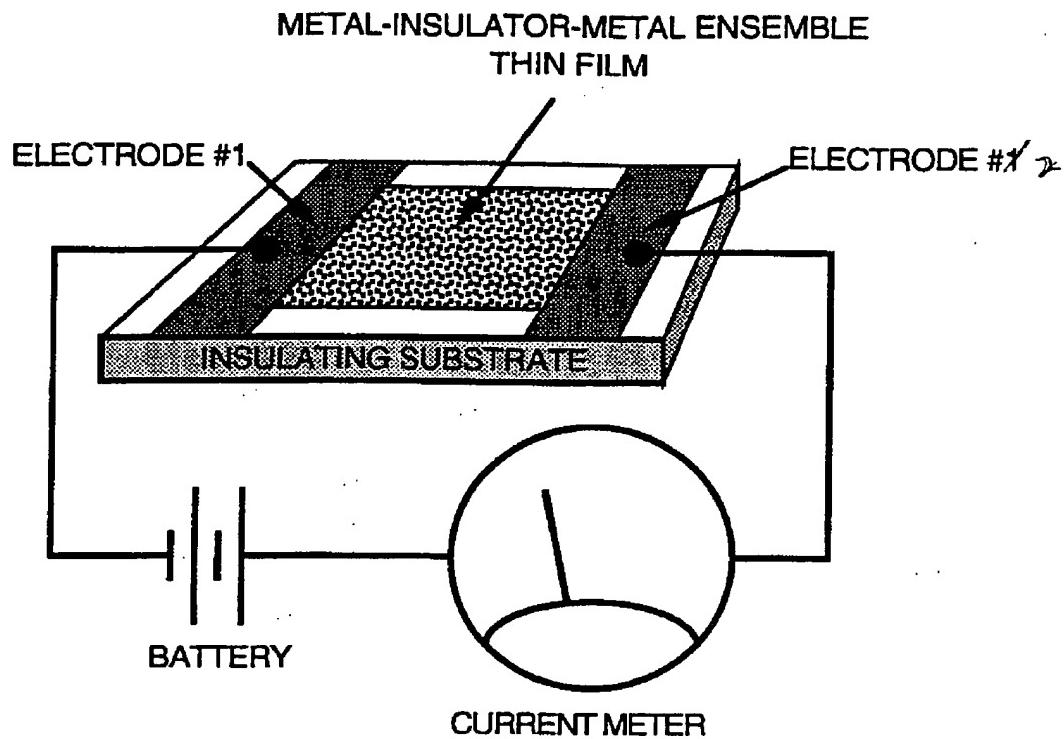


FIGURE 2.

WITNESSED AND UNDERSTOOD: D. Fleckan DATE: 6/11/97

WITNESSED AND UNDERSTOOD: William R. Bangs Jr. DATE: 6/12/97

CHEMICAL SENSOR

TEMPERATURE COMPENSATED
VOLTAGE OUTPUT RELATED TO
CHEMICAL CONCENTRATION

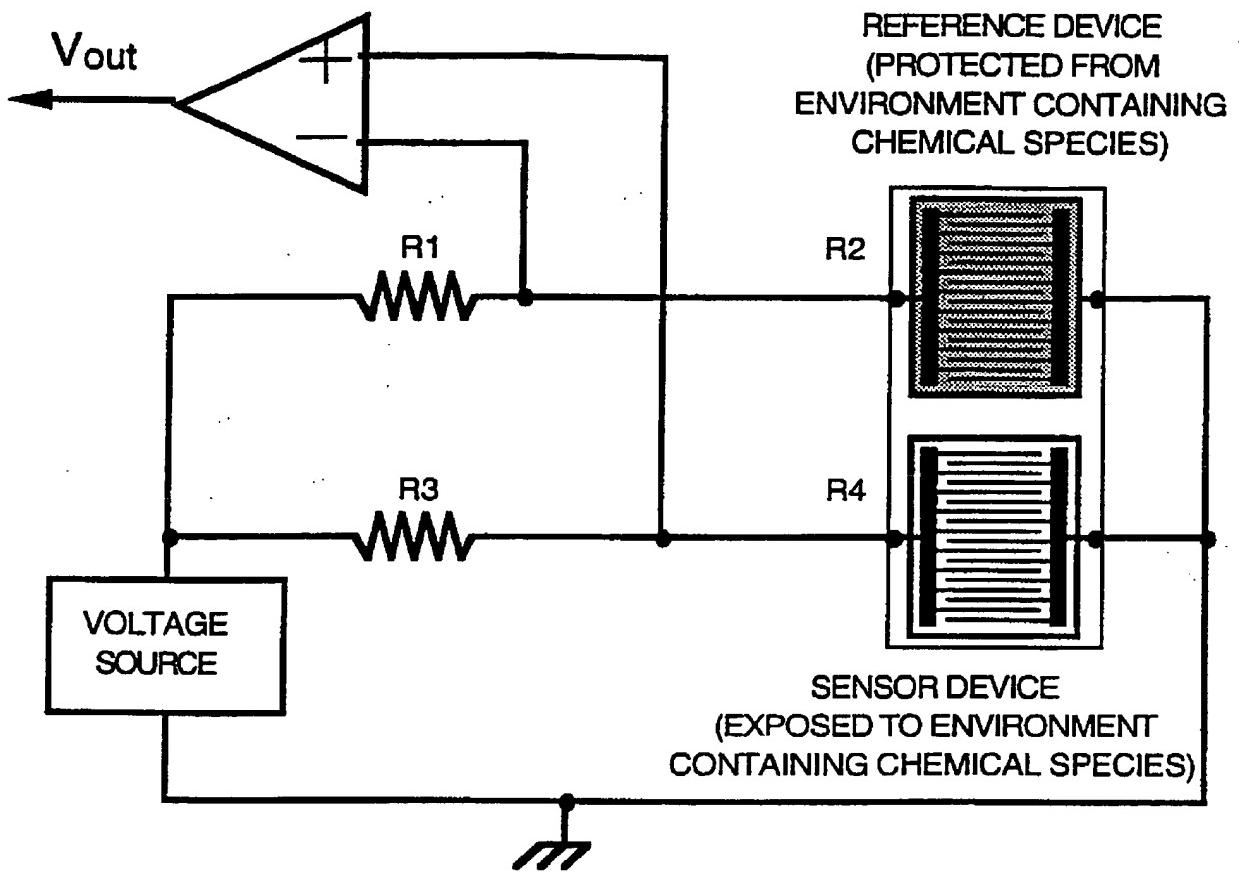


FIGURE 3.

WITNESSED AND UNDERSTOOD: R. Freehan DATE: 6/11/97

WITNESSED AND UNDERSTOOD: William R. Bagby DATE: 6/12/97

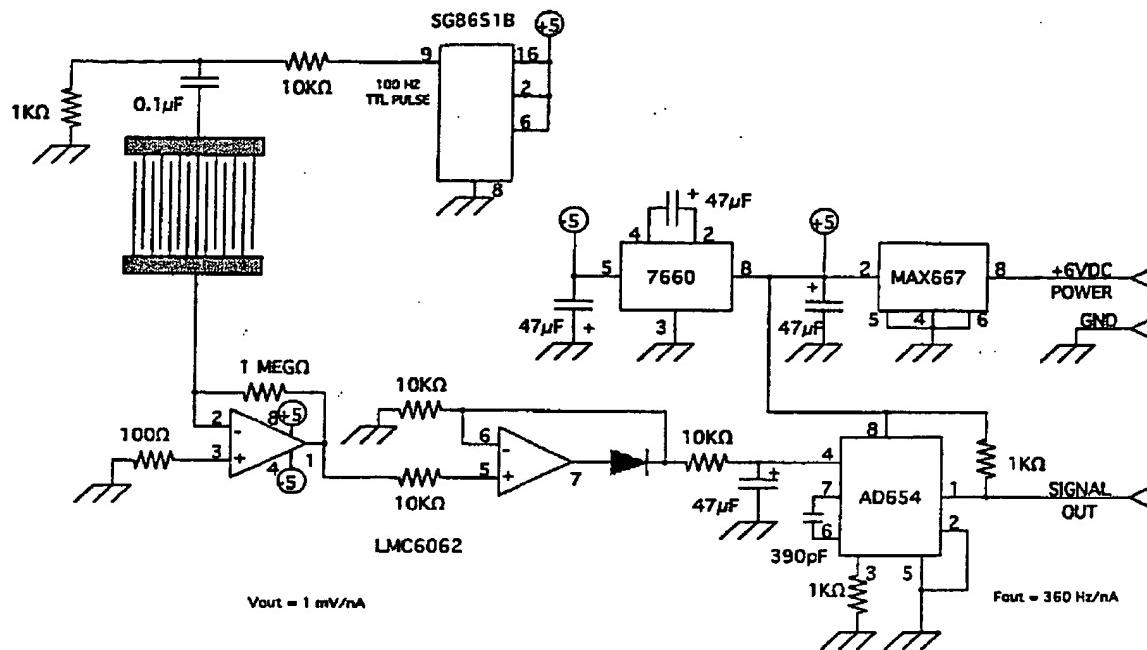


FIGURE 4.

WITNESSED AND UNDERSTOOD: D. Shleikan DATE: 6/11/97WITNESSED AND UNDERSTOOD: William R. Basch DATE: 6/12/97

A typical MIME device chemical sensor has a film thickness of 0.1 to 1 μm (i.e., 1,000 - 10,000 \AA). The composition of the MIME thin film and the geometry of the electrode on which it is deposited, are selected to provide an attractive baseline resistance (e.g., 10,000 Ω) to permit high precision measurement of resistance changes with simple electronic circuitry. Exposure of the film to low concentrations (e.g., 100 ppm by volume) of chemical vapors can change the resistance by several percent. This is a very large change if temperature effects can be nulled out by using a reference device such as the one disclosed in this invention. Indeed, it is quite easy to measure resistance changes of 1 part in 10⁵ (i.e., $\pm 0.001\%$) with this sensor/reference combination. Thus, monitoring trace levels (e.g. sub-ppm) concentrations of many vapors is readily achievable.

The linearity and sensitivity of the MIME sensor are illustrated in figures 5 through 9. In this case a gold core having a nominal radius of 1 nanometer was combined with an alkanethiol ligand shell having 8 carbon atoms in the alkane chain. A film of this material approximately 0.4 micrometers in thickness was sprayed onto a small interdigital electrode consisting of 50 "finger pairs" of gold 15 μm wide and spaced 15 μm from the next electrode. The finger aperture was 4800 μm . The gold microelectrode was lithographically fabricated on an insulating substrate of quartz. The electrode coated with the metal-insulator-metal ensemble was excited with an AC square wave having an amplitude of 5 V and a frequency of 100 hz (figure 4.). Current flowing through the device was converted into a voltage (using a current-to-voltage converter). The resulting AC voltage was rectified and filtered and then presented to a voltage to frequency converter. Thus, AC conductance changes in the device were converted into frequency changes that were easily recorded using a laboratory data acquisition system. This approach is not necessary in order to practice this invention but it was convenient for our particular laboratory set-up.

The relative resistance change of the device upon exposure to toluene vapor is illustrated in figure 5. The responses are astonishingly rapid and reversible. Figure 6 illustrates the highly linear behavior of the device over a wide range of concentrations. Figure 7 shows the ability of the MIME sensor to detect trace

WITNESSED AND UNDERSTOOD: R. P. Keehan DATE: 6/11/97

WITNESSED AND UNDERSTOOD: William R. Basch DATE: 6/12/97

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quantities (e.g., sub parts-per-million by volume concentration) of toluene vapor. Figure 8 compares the sensitivity of the device to a variety of other vapors. Of great significance is the extraordinarily low response to water vapor which is essential for practical applications in which trace levels of organic vapors must be detected and monitored in humid ambient air.

WITNESSED AND UNDERSTOOD: D. Schaefer DATE: 1/17/97

WITNESSED AND UNDERSTOOD: William R. Borgby DATE: 6/12/97

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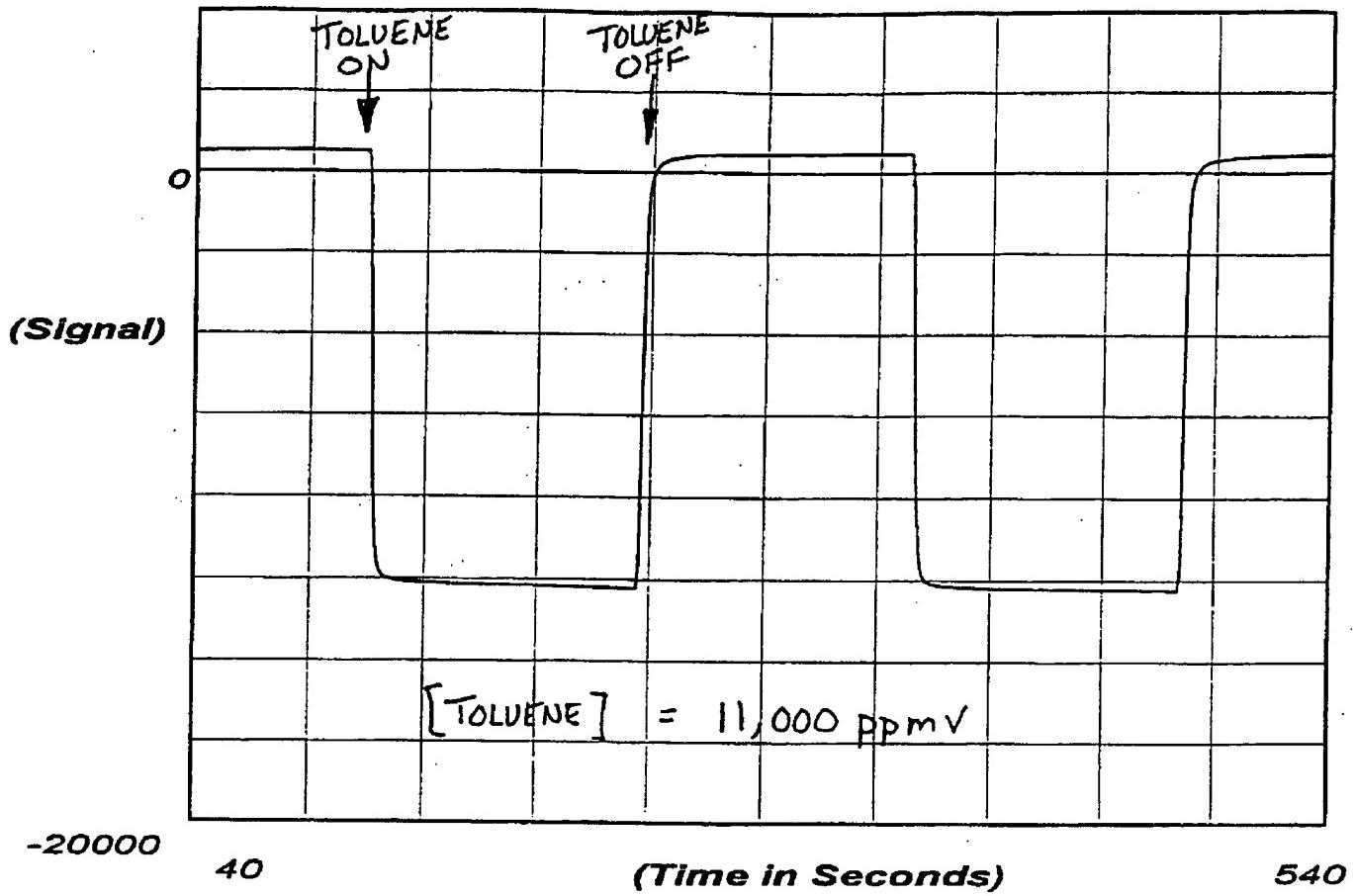


FIGURE 5.

WITNESSED AND UNDERSTOOD: D. Fletcher DATE: 6/11/97WITNESSED AND UNDERSTOOD: William R. Baumhauer DATE: 6/12/97

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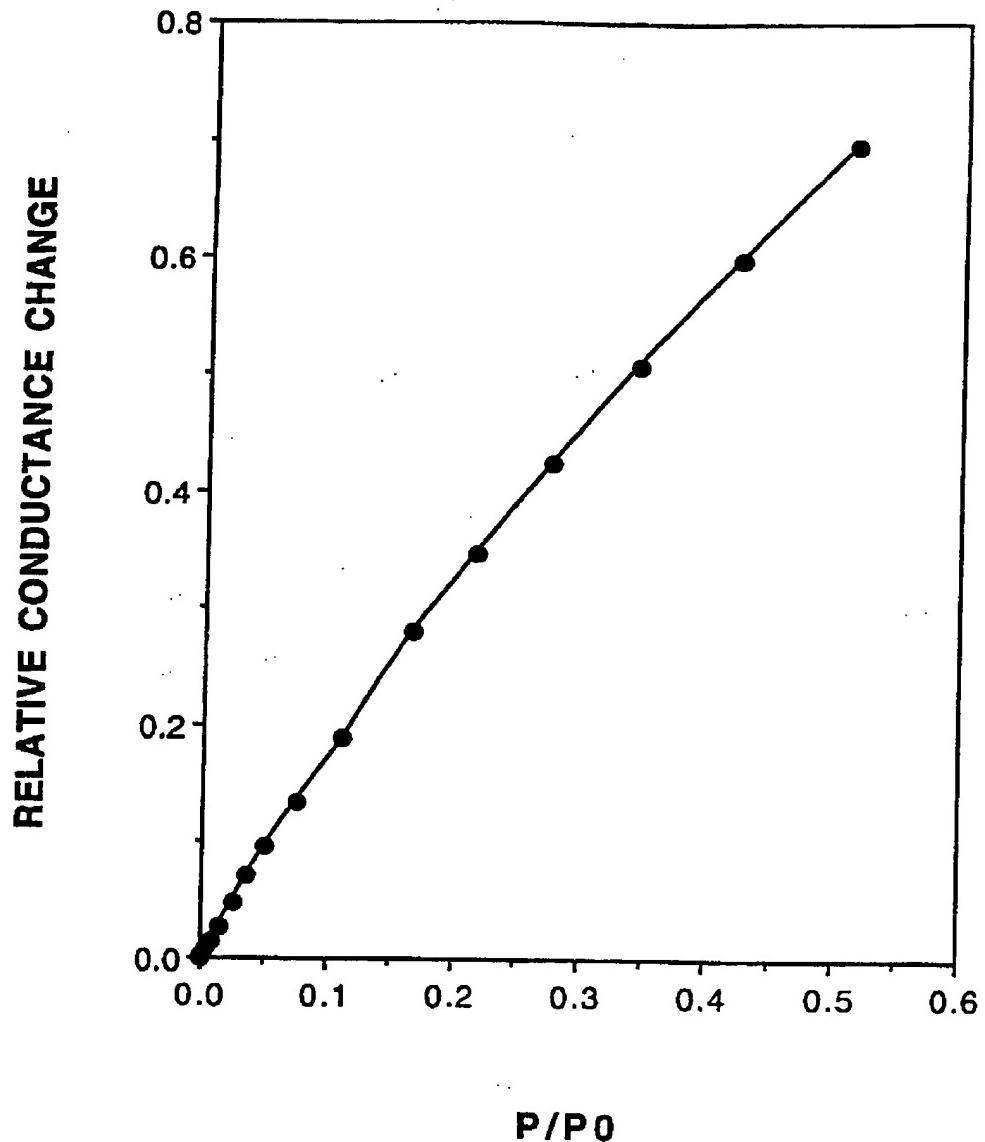
C8(1:1) REONSE TO TOLUENE VAPOR

FIGURE 6.

WITNESSED AND UNDERSTOOD: John R. Reehan DATE: 6/11/97WITNESSED AND UNDERSTOOD: William R. Basye Jr. DATE: 6/12/97

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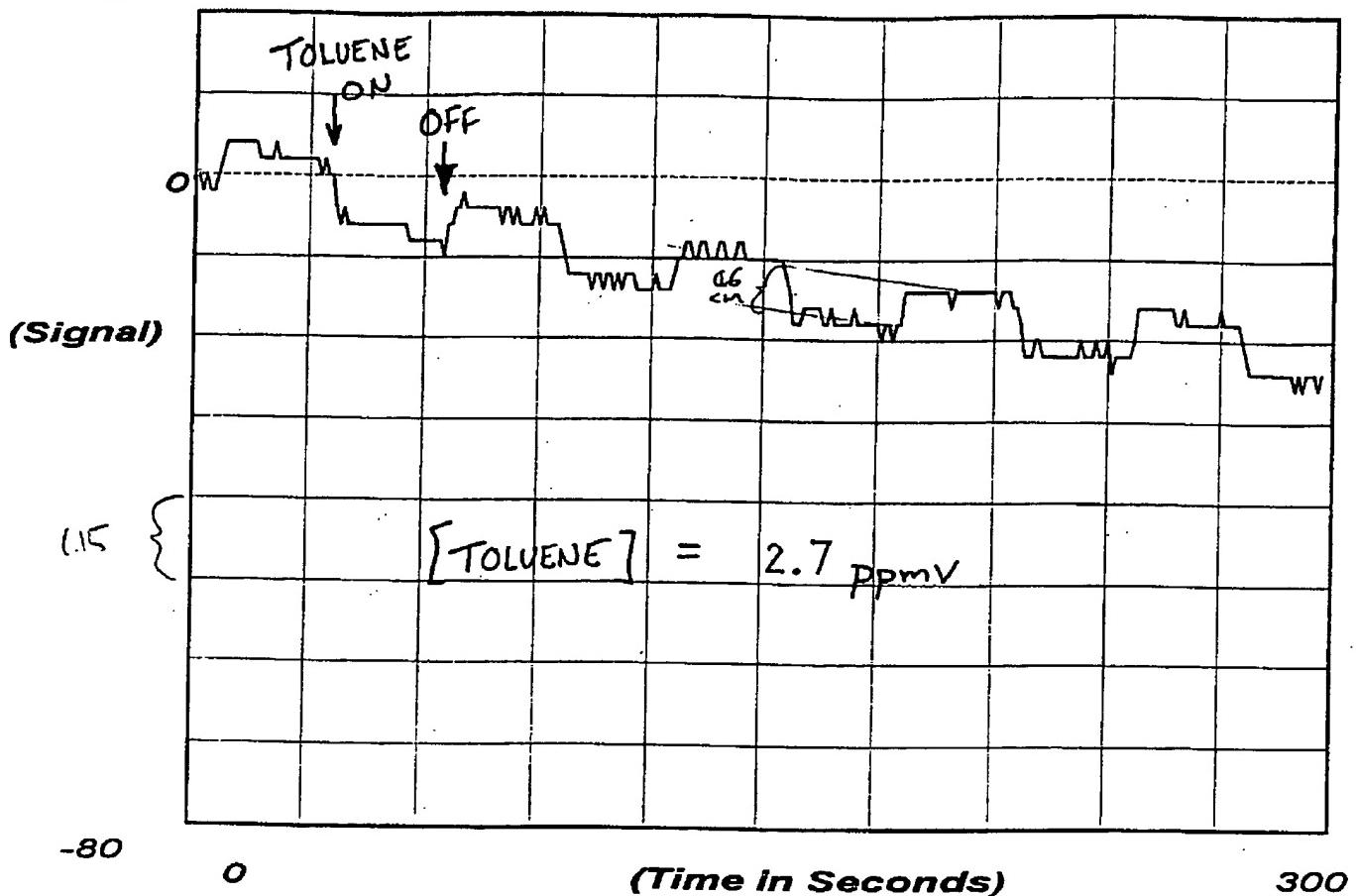
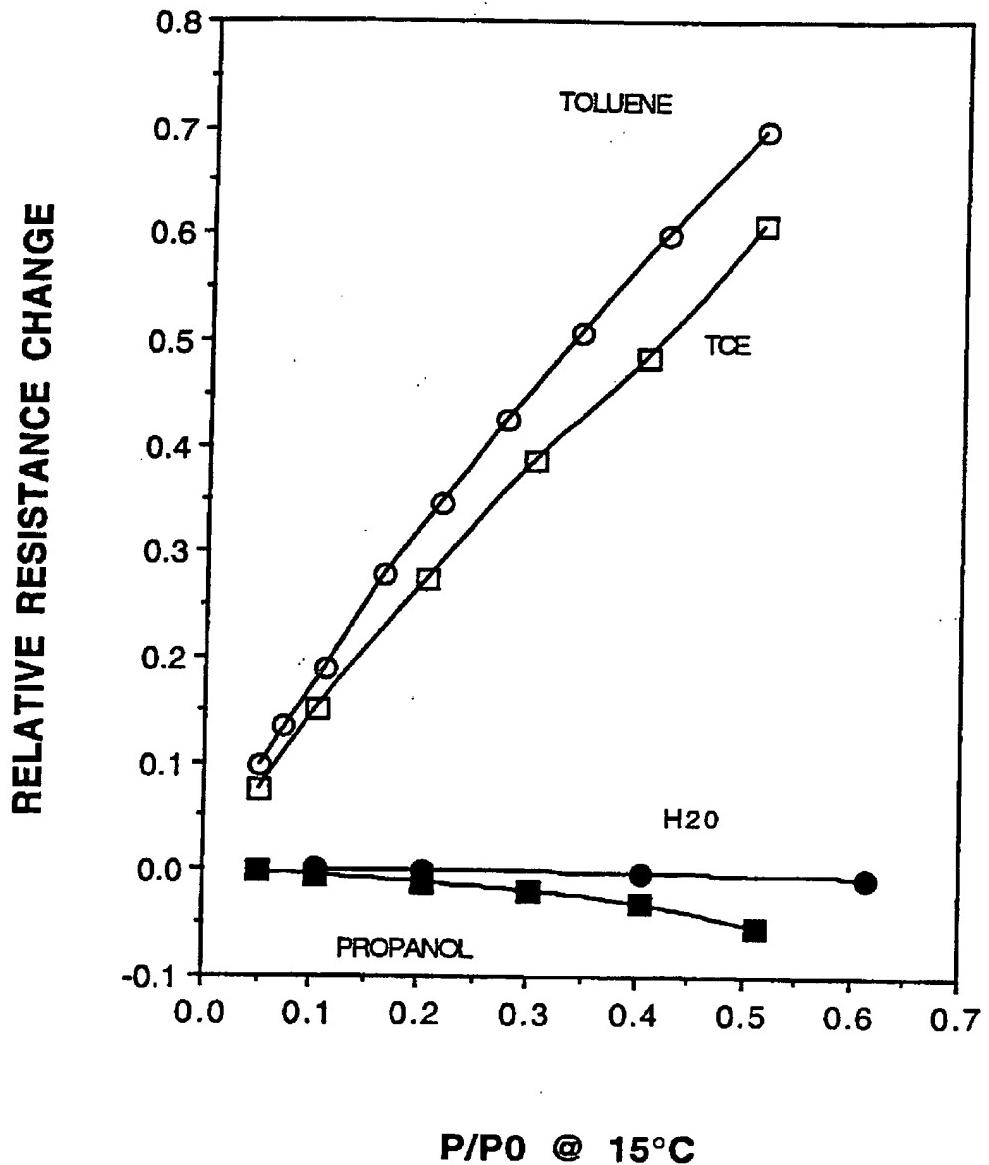


FIGURE 7.

WITNESSED AND UNDERSTOOD: D. Michael DATE: 6/11/97WITNESSED AND UNDERSTOOD: William R. Bayly DATE: 6/12/97

C8(1:1) RESPONSE TO VARIOUS VAPORS**P/P₀ @ 15°C****FIGURE 8.**WITNESSED AND UNDERSTOOD: R. S. Reehan DATE: 6/11/97WITNESSED AND UNDERSTOOD: William R. Bayard DATE: 6/12/97

SPECIFIC ADVANTAGES AND NEW FEATURES:

The chemical sensor described in this disclosure has numerous advantages:

- 1) It is very simple.
- 2) It is very rapid, linear, and reversible in response.
- 3) Variations in the film composition (e.g., metal core size or type, ligand shell size or type) permit adaptation to a large variety of chemical monitoring problems.
- 4) It is very sensitive.
- 5) It can be made very small.
- 6) It can be manufactured very inexpensively.
- 7) It is readily interfaced to inexpensive electronic readout devices.
- 8) It is temperature compensated using a reference sensor.
- 9) It is tolerant of production variations.
- 10) It requires very little electrical power.
- 11) It is very rugged.
- 12) It can work in many environments (i.e., porous solid, liquid, gas).

WITNESSED AND UNDERSTOOD: D. Fleck Jr. DATE: 6/11/97

WITNESSED AND UNDERSTOOD: William R. Baumgat DATE: 6/12/97

ALTERNATIVE EMBODIMENTS:

As described in the preceding sections, the sensor can be made from a wide variety of electrically conductive colloidal sols. Of particular interest is the chemical structure of the ligand shell which can be tailored to provide a diverse range of specific chemical interactions useful to make the chemical sensor selective.

There are no critical geometrical constraints in the device design, although it is very desirable to use thin films so that the chemical analyte can rapidly diffuse into the film to cause a rapid response. This disclosure describes a sample and reference, or "half-bridge" configuration of the sensor. A fully balanced Wheatstone bridge configuration having 4 devices would also work very well. As stated previously, either AC or DC excitation of the device is acceptable.

WITNESSED AND UNDERSTOOD: D. Fleckham DATE: 6/11/97

WITNESSED AND UNDERSTOOD: William R. Beaudy DATE: 6/11/97

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EXECUTION:**INVENTOR(S)**

Disclosed by: _____ (Inventor) Date: _____

(Co-Inventor) Date: _____**WITNESSES**Disclosed to R. Sheehan and understood by me on 6/11/97
(WITNESS) (DATE)Disclosed to William R. Bangs and understood by me on 6/12/97
(WITNESS) (DATE)WITNESSED AND UNDERSTOOD: R. Sheehan DATE: 6/11/97WITNESSED AND UNDERSTOOD: William R. Bangs DATE: 6/12/97

Ref:

**SIZE INDUCED METAL TO SEMICONDUCTOR TRANSITION IN A
STABILIZED GOLD CLUSTER ENSEMBLE**

Arthur W. Snow
U.S. Naval Research Laboratory
Code 6120
Washington, D.C. 20375

and

Hank Wohltjen
Microsensor Systems, Inc.
62 Corporate Ct.
Bowling Green, KY 42103

Organic ligand stabilized metal clusters are a unique composite system possessing nanometer scale domains in which a metal core is encapsulated by an insulating organic monolayer. The confinement of a group of neutral metal atoms in such a small domain confers electronic properties that may be intermediate between continuous metals and quantized molecular species depending on the actual size of the domain. The insulating monolayer encapsulant is a conductivity barrier through which facile electron tunneling and/or hopping occurs. As a composite, both domains can exert strong influences in the macroscopic electrical conductivity. The strengths of these influences depend on their intrinsic nature and dimensions of each domain. Such materials are postulated to have exciting prospects for applications in microelectronics and possibly molecular electronics.[1] Our interest is in the development of these materials as the responsive component in a microelectronic chemical vapor sensor. In preparing and characterizing several series of these

materials with variable core sizes and ligand shell thicknesses, we have observed a transition from a positive to a negative temperature coefficient of electrical conductivity for thin films of a homologous series of alkanethiol stabilized gold clusters as described below and illustrated in Figures 1 and 2.

As a model system, alkanethiol stabilized gold clusters have a chemistry that is very amenable to systematic variation in both size of the gold core and thickness of the ligand shell. They are easily dispersed to concentrations as high as 10% by weight in nonpolar organic solvents and can be manipulated and characterized as soluble organic compounds. Recently, a synthesis of elegant simplicity was reported for this system where a nanometer scale gold cluster derivatized with a monolayer of dodecanethiol is described.[2] In this two phase system, gold chloride is dispersed by a phase-transfer agent in a toluene solution of the alkanethiol and is subsequently reduced by contact via rapid stirring with an aqueous sodium borohydride solution. As neutral gold particles nucleate and begin to grow, they are sequestered by a monolayer of the alkanethiol in a kinetically controlled fashion. We have found that simple variation of the gold:alkanethiol stoichiometry can generate stabilized clusters with a large range of gold atoms in the core and have prepared such a series of dodecanethiol stabilized gold clusters (see Table 1). As an abbreviated nomenclature for the normal alkanethiol stabilized gold cluster we use the following general form: Au:C_n(X:Y) where the subscript n denotes the number of carbon atoms in the alkane chain and (X:Y) denotes the gold:alkanethiol stoichiometric ratio. As

practical limits to desirable variations, the lower limit is where the electrical conductivity becomes very low and difficult to measure (e.g. X:Y = 1:3 for the dodecanethiol system) and the upper limit is where the core approaches a size too large for the shell to solublize (e.g. X:Y = 8:1 for the dodecanethiol system).

~~Some~~ very thorough characterization of the Au:C₁₂(1:1) cluster size has been reported along with a very useful spherical model relating the core size to the alkanethiol coverage. [3] For this particular cluster, the core has a radius of 1.1 nm and two of three gold surface atoms (assuming a hexagonal closest packed arrangement) are functionalized with a chemically bonded alkylthiolate. We have employed this model with our thermogravimetric analysis (TGA) measurements to calculate the core radii for the other members of the Au:C₁₂(X:Y) series. The results are presented in Table 1.

Direct current conductivity measurements were made on films approximately 0.4 microns thick deposited on an interdigital microelectrode [4] (see Table 1). There is a regular increase in the conductivity with increasing gold core size. The conductivity dependence on deposition thickness is nearly linear over a 0.03 to 0.7 μ range and Ohm's Law was followed over a +/- 1 volt range. The temperature dependence of the conductivity is presented in Figures 1 and 2. The Arrhenius plot shows the magnitudes to which the gold core size and temperature variation modulate the level of conductivity. The data for the Au:C₁₂(1:1) member of the series is

very close to being linear in this plot, and its slope yields an activation energy of 15.8 kJ/mol which is in good agreement with the 16 kJ/mol reported for this cluster [3]. However, the nature of the conductivity temperature dependence is not well represented by the Arrhenius plot.

Figure 2 presents a simple linear scale conductivity vs. temperature plot where the conductivity of each cluster deposition is normalized to its value at 20°C. This causes a common crossover point at 20°C and, as a practical point, illustrates susceptibility to thermal fluctuations at room temperature. If it is assumed that the dodecanethiol ligand shell thickness does not vary from member to member of this series, then the systematic variation in gold core size displays a most interesting effect on the temperature dependence of the electrical conductivity. At temperatures from 0 to 20°C this effect progresses from a thermally activated semiconductor type dependence to a thermally deactivated metallic type dependence as the core size increases. Looking at the entire temperature range of these data, it is apparent that this transition emerges as a maximum at low temperatures for clusters with larger core sizes.

As mentioned above, there appear to be at least two processes, one thermally activating the other thermally deactivating, influencing the conductivity of this composite ensemble. We would speculate to associate the deactivating process with the metal core and the activating process with the ligand shell. Two mechanisms are conceivable as relating to the core size effect. First is a "size

induced metal-insulator transition" which relates to the effect on core conductivity as the core size shrinks to the domain of the de Broglie wavelength, the decrease in conductivity being approximately in proportion to the third power of the particle diameter.[8] While we do not observe a slope corresponding to the third power dependence in a log-log plot of the core radius-conductivity data in Table 1, the trend of a decreasing conductivity with core size is certainly there. The second mechanism has to do with the effect of the core size on the charging energy barrier to tunneling. It has been shown by low frequency AC measurements that an increase in gold cluster radius (0.72 nm to 10 nm) strongly diminishes this barrier (0.3 eV to 0.01 eV).[9] Thus, with increasing core size, the conductivity of the core becomes more metallic in nature while the tunneling through the ligand shell becomes more facile. These mechanisms would appear to be qualitatively consistent with the data in Figure 2.

The ligand shell thickness manifests a very strong effect on electrical conductivity as a resistance barrier between contacting metal clusters. This effect has been reported for ligand shell thicknesses corresponding to normal alkanethiol carbon chain lengths of 8, 12 and 16 where a dramatic conductivity decrease of two orders in magnitude for each tetramethylene increment in thiol chain length was observed. [3] We have found that these ligand shell thickness effects superimpose on the cluster core size effect described above and we are currently completing a two dimensional (i.e. core size and ligand shell thickness) property map with gold core

radii ranging from 0.6 to 3.6 nm and alkanethiol chain lengths ranging from 4 to 16. This will be reported in detail in the near future. [7]

References and Notes

1. Schon, G.; Simon, U. *Colloid Polym. Sci.* **1995**, *273*, 101.
2. Brust, M.; Walker, M.; Bethell, D.; Schiffrian, D.J.; Whyman, R. J. *Chem. Soc., Chem. Commun.* **1994**, 801.
3. Terrill, R.H.; Postlethwaite, A.; Chen, C-H.; Poon, C-D.; Terzis, A.; Chen, A.; Hutchison, J.E.; Clark, M.R.; Wignall, G.; Londono, J.D.; Superfine, R.; Falvo, M.; Johnson Jr., C.S.; Samulski, E.T.; Murray, R.W. *J. Am. Chem. Soc.* **1995**, *117*, 12537.
4. The interdigital electrode (MSI 302 device, Microsensors Systems Inc.) is an electrode array consisting of 50 finger pairs (n) with the following dimensions: spacing (d), 15 micron; finger width, 15 micron; overlap length (L), 4800 microns; electrode thickness, 1500Å. For an electrode of this geometry the conductivity of a film deposited on it is related to the film thickness (h), current (I) and voltage (V) as follows: [5,6]

$$\sigma = [d/(2n-1)L] [1/h] [I/V]$$

This electrode geometry is designed for measurement on thin films the thickness of which should not greatly exceed that of the electrode (i.e. not greater than a factor of 10) since the electric field rapidly diminishes at distances greater than this factor above the plane of

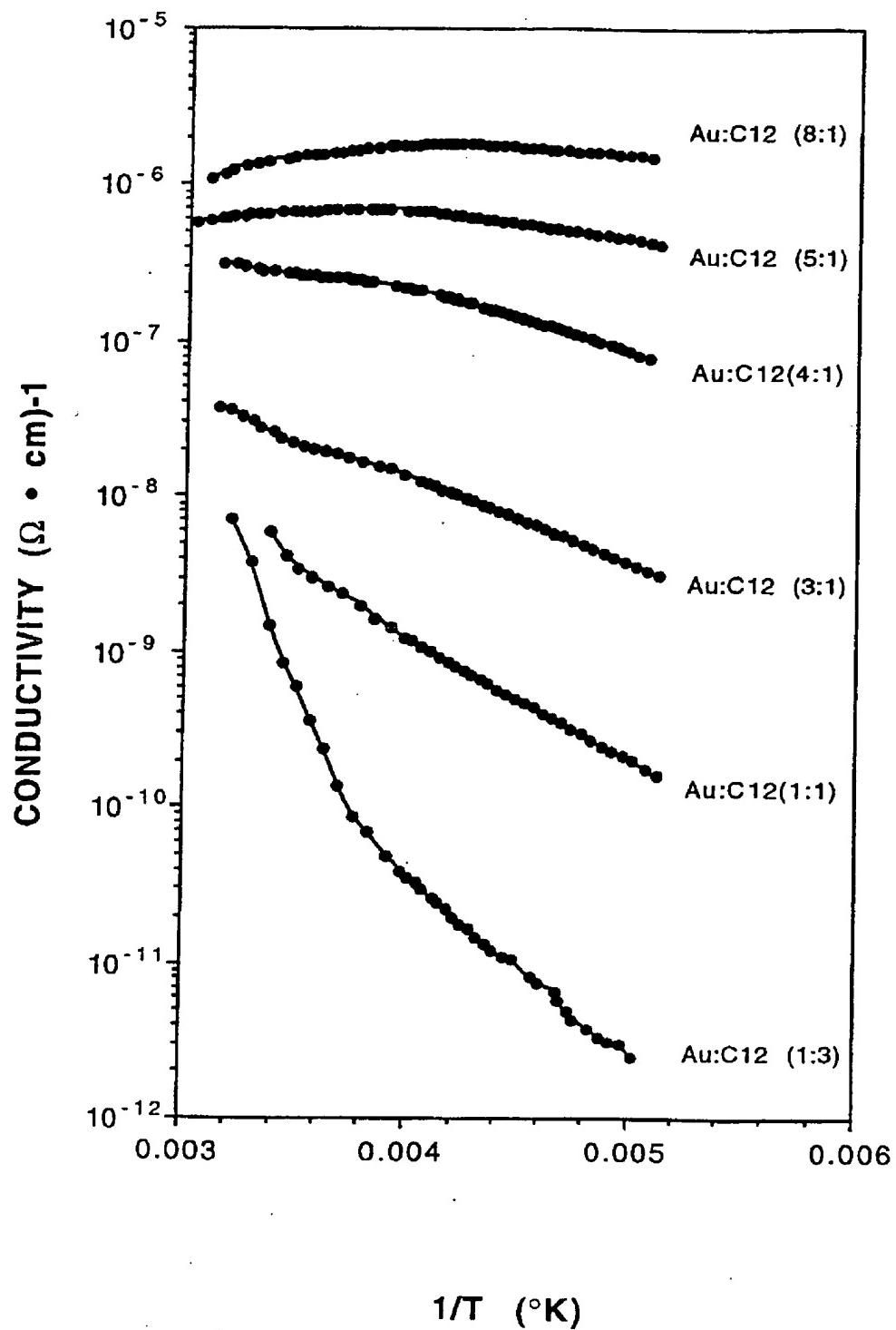
the electrode. This analysis will be presented in detail in a future publication. [7]

5. Wohltjen, H.; Barger, W.R.; Snow, A.W.; Jarvis, N.L. *IEEE Trans. Electron. Devices*, 1985, ED-32(7), 1170.
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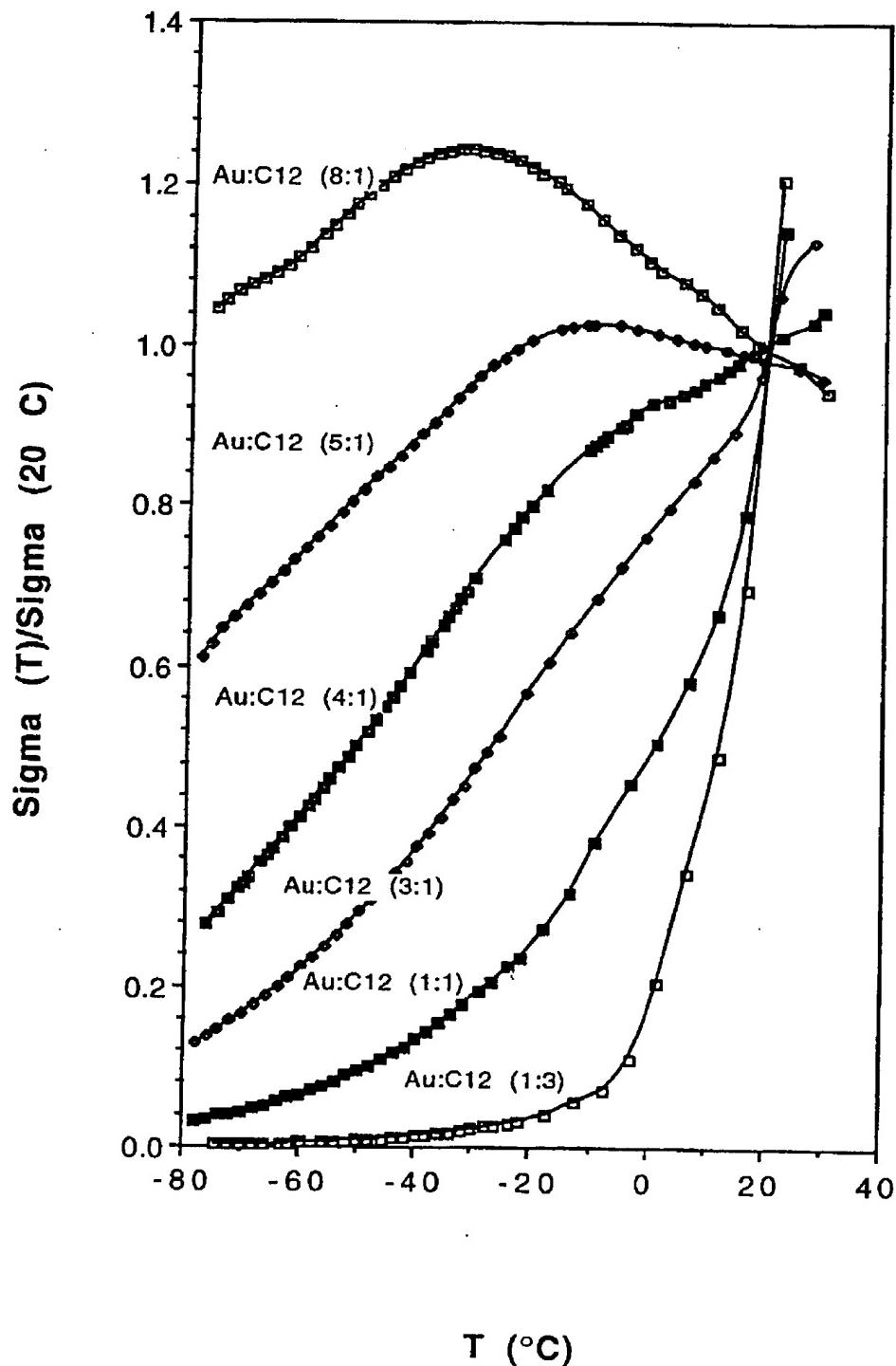
Table 1. Characterization of the Au:C₁₂(X:Y) Cluster Series

X:Y	1:3	1:1	3:1	4:1	5:1	8:1
W _{Au}	0.7195	0.7549	0.7957	0.8427	0.8709	0.8947
R _{core} (nm)	0.86	1.14	1.56	2.29	2.97	3.61
Au atoms/core	155	360	922	2920	6370	11400
σ _{20°C} (Ω cm) ⁻¹	2x10 ⁻⁹	1x10 ⁻⁸	5x10 ⁻⁸	2x10 ⁻⁷	1x10 ⁻⁶	3x10 ⁻⁶

Data from "C12(X,Y) 1/T vs sigma"



Data from "C12(X,Y) T vs I(T)/I(20)"



**METAL-INSULATOR-METAL ENSEMBLE (MIME)
CHEMIRESISTOR SENSOR**

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and

Arthur W. Snow
U.S. Naval Research Laboratory
Code 6120
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A chemiresistor is a simple solid-state device whose electrical resistance is changed by the presence of a chemical species. They typically incorporate a thin film of a semiconducting material deposited onto a pair of contacting electrodes. [1] Reports of such devices date back to the 1960's [2], and thin films of organic [3] and polymeric [4] materials have been employed as transducers. Typically, the interaction between the vapor and semiconductor involves a transfer of charge that strongly affects the number of electrons in the conduction band of the semiconductor film. The requirement for charge transfer limits the sensor response to

suitable electron donor or acceptor species which may or may not be reversible depending on the strength of the interaction. More recently, Lewis et.al. have reported on a novel chemiresistor device that relies on measurement of electrical conductivity changes caused by vapor induced swelling of polymers loaded with carbon black [5].

In this correspondence we describe a fundamentally new type of chemiresistor that operates by a different mechanism. The transducer thin film incorporates an ensemble of nanometer size metal particles each coated by an organic monomolecular layer. The combination of a large, three dimensional assembly of these colloidal size, conducting metal cores separated by very thin insulating shells has led us to refer to this device as a "Metal-Insulator-Metal Ensemble" (or "MIME") device. Our purpose in this study was to demonstrate its speed, reversibility, sensitivity and selectivity of the MIME device in detecting organic chemical species.

As a model system for the MIME component we use an alkanethiol stabilized gold nanocluster material. This system has a chemistry that permits controlled and facile variations to be made in the size of the gold core and thickness of the ligand shell. These clusters are very stable in the solid-state and easily re-disperse in nonpolar organic solvents at concentrations up to 10% by weight. The synthetic method for preparation of these clusters is elegantly simple involving reduction of gold chloride in the presence of alkanethiol surface complexing agents [6]. Variation of the gold:alkanethiol stoichiometry has a pronounced effect on the core

size which in turn has a dramatic effect on the electrical conductivity and its temperature dependence [7]. The thickness of the ligand shell as determined by the number of carbon atoms in the alkanethiol chain also has a strong influence on the level of conductivity. [8] As an abbreviated nomenclature for these normal alkanethiol stabilized gold clusters we use the following general form: Au:C_n(X:Y) where the subscript n denotes the number of carbon atoms in the alkane chain and (X:Y) denotes the gold:alkanethiol stoichiometric ratio used in the synthesis. The individual clusters Au:C₈(1:1), Au:C₁₂(1:1) and Au:C₁₆(1:1) have received a very thorough physical characterization. [7]

Here we describe the fabrication and response characteristics of the Au:C_n(X:Y) MIME device to a series of four vapors (toluene, tetrachloroethylene, 1-propanol and water) using the Au:C₈(1:1) cluster as a representative transducer film.

EXPERIMENTAL SECTION

Synthesis. Au:C₈(1:1). The procedure is closely related to that of refs. 5 and 7. Triple distilled water and HPLC grade toluene were used as solvents. The following solutions were prepared in acid cleaned glassware: (C₈H₁₇)₄NBr (4.56 g, 83.4 mmol)/toluene (167 ml); HAuCl₄.3H₂O (0.8025 g, 2.04 mmol)/water (62.5 ml); 1-octanethiol (0.297 g, 2.03 mmol)/toluene (2 ml); NaBH₄ (0.787 g, 20.8 mmol)/water (52.5 ml). The HAuCl₄/water was added to the (C₈H₁₇)₄NBr/toluene solution with vigorous stirring. After 2 min

with continued vigorous stirring, the octanethiol/toluene solution was added followed by the NaBH₄/water solution during which rapid color development occurred. Vigorous stirring was continued for 3 hr. The toluene phase was then separated, concentrated (55°C/60 mm) to an approximate 10 ml volume. The product was precipitated by dropwise addition into 800 ml rapidly stirred ethanol. After settling overnight at 10°C, the clear supernate was decanted, and the settled product was collected by centrifugation followed by washing with fresh ethanol and drying. This crude product was redissolved in 3 to 4 ml toluene and reprecipitated by dropwise addition into 200 ml rapidly stirred ethanol. After standing 12 hr at 10°C, the 200 ml suspension is centrifuged (6000 rpm), and the collected product was washed with fresh ethanol and vacuum dried. Yield 0.39 g (79%).
TGA analysis: N₂ atm 600°C mass loss 19.35% (lit. [7] 19.74%).

Sensor and Circuit Configuration. The sensor was fabricated by deposition of a thin film of the Au:C₈(1:1) cluster onto an interdigital microelectrode. This microelectrode (Microsensor Systems, Inc. P/N 302) is a gold electrode array fabricated on a 7 x 12.5 x 1 mm quartz substrate and consists of 50 finger pairs with the following dimensions: spacing, 15 microns; finger width, 15 microns; overlap length, 4800 microns; electrode thickness, 1500 Å. This device was mounted on a brass plate heated to 120°C and coated with a 0.2 to 0.4 micron thick Au:C₈(1:1) cluster film. Film deposition is accomplished using an airbrush technique where a 10 mg/ml chloroform solution was sprayed using a fine nozzle setting for 16 passes of one second duration. The film thickness estimate

was made by calculation from gravimetric measurement of the film mass (assuming a density of 3 g/cm³) and is accurate to only one significant figure.

Conductivity changes in the microelectrode were measured using an AC technique. A square wave potential of 5 volts and a frequency of 100 Hz was used to excite the microelectrode. The resulting current in the microelectrode was processed using a current-to-voltage converter circuit followed by a precision rectifier and low-pass filter. Thus, the magnitude of the 100 Hz AC microelectrode current was converted into a proportional DC voltage. For convenience, this voltage was converted to a frequency (using a V/F converter) to allow data acquisition over a wide dynamic range using a computerized frequency counter. This measurement scheme allowed the microelectrode current to be measured, displayed, and stored with a time resolution of one second and a relative current resolution of 0.001%

Vapor Response. The sensor was mounted in a custom made gold plated aluminum cell designed for low dead volume (i.e., < 0.5 cc) with intake and exhaust ports positioned immediately above the electrode and connected to the circuit by way of pogo pin contacts to the contact pad of the electrode. Vapors of toluene, tetrachloroethylene, 1-propanol and water were generated from bubblers at 15°C, diluted with dry air to desired concentrations and delivered to the cell on an alternating exposure-purge schedule by a

computer controlled vapor generator (Microsensor Systems Inc. model VG7000).

RESULTS AND DISCUSSION

The Au:C_n(X:Y) MIME sensor device is fabricated by deposition of a thin film onto an interdigital microelectrode which is then connected to an AC measurement circuit. Fairly simple measurement electronics are possible when the MIME device has a resistance in the range of 1 KΩ, to 100 MΩ so attention was paid to selection of a Au:C_n(X:Y) cluster whose thin film resistance fell into this range. The Au:C₈(1:1) cluster was selected for its midrange device resistance (ca. 1.5 MΩ) and its representative response to vapors selected for study.

Coatings were deposited by spray deposition from a chloroform solution onto a microelectrode held at a temperature of 120°C. The elevated temperature promotes a more uniform film formation. The liquid chloroform evaporating from the electrode surface at room temperature leaves a film composed of coarse rings from evaporation of the original droplets. By increasing the electrode temperature well above the chloroform boiling point, this solvent is rapidly flashed away, and we believe to some extent a "sintering" occurs between the waxlike ligand shells of the clusters.

Vapor induced conductivity changes in the MIME device were measured using an AC square wave excitation. The AC circuit is used to eliminate problems with a small resistance drift observed during a

DC measurement which we believe is a result of slow electromigration of the nanoclusters to the electrode surface.

The set of vapors selected for this initial characterization study include toluene, tetrachloroethylene, 1-propanol and water. The intent of the survey is to include a hydrocarbon, a chlorocarbon, a hydrogen bonding polar organic and a very polar inorganic, all of which have similar vapor pressures. Similar analyte vapor pressures allow a more direct comparison of the chemical selectivity afforded by the nanocluster (i.e. at the sensor temperature the vapor pressures of each vapor are nearly equal so that chemical interactions rather than simple physical vapor activity are the main determinant of any sensor selectivity).

The sensor response to five 60 sec exposure/purge cycles of toluene vapor at high (11000 ppm) and low (2.7 ppm) concentrations are presented in Fig. 1. Toluene vapor exposure causes a large and rapid decrease in the conductance of the sensor. Greater than 90% of the signal response occurs within 1 sec of its 30 sec exposure. The recovery is equally rapid and complete. The lower portion of Fig. 1 indicates detection limits well below one ppmv are achievable.

The response isotherm to the set of four vapors over a very broad concentration range is displayed in Fig. 2. The inset depicts this response at the very low end of this concentration range for toluene and TCE. The response to toluene and TCE vapors is very large and deviates slightly from linearity with the slope of the curve

becoming greater at the low end of the concentration range. The sensor is remarkably unresponsive to water vapor even at high concentrations. The lack of water sensitivity is of great importance for practical environmental sensing applications. Propanol vapor produces the unexpected result of a small conductance increase which occurs only at very high vapor concentrations.

A simplified schematic representation of the MIME nanocluster structure is offered in Fig. 3. While we have not completed our investigations into the details of the electronic charge transport mechanism of the MIME device, we believe that electron transport probably occurs via at least two mechanisms; namely tunelling between the metal cores (since the cores are spaced less than 2 nm apart and the cores themselves have a nominal diameter that is smaller than the DeBroglie wavelength of electrons in the gold core); and hopping along the atoms of the thiol-alkyl ligand. Anything that perturbs the charge distribution on the gold core or the thiol-alkyl ligand (e.g., adsorbed vapors) is likely to have a profound effect on both the tunnelling current and the electron hopping current. Swelling of the MIME "lattice" by absorbed chemicals is also likely to have a profound effect on tunelling currents. Another interesting feature of the MIME morphology is the likely presence of regular interstitial void spaces around the nanoclusters. This void space permits the very rapid diffusion of chemical species into the nanocluster ensemble.

The overall performance of the MIME chemiresistor is exceptionally good. The sensitivity to some vapors (e.g., toluene and tetrachloroethylene) is high enough to permit detection limits significantly below 1 ppmv. Simple changes to the device and electronic configuration will likely afford very significant improvements in sensitivity. The simplicity and low power requirements of the device combined with the astonishingly small response to water vapor makes it very attractive for simple, portable vapor monitoring systems. Few solid-state chemiresistors have ever exhibited reversible response times as rapid as the MIME devices reported here. Reproducibility, stability, and processibility of the alkanethiol stabilized gold nanocluster materials have been excellent. The tailoring of this model system by adding specific chemical functionalities to the ligand shell is an obvious and facile way to adjust the selectivity and sensitivity for a wide variety of chemical analytes in both condensed and vapor phase. Currently, we are completing a study of the role that the gold core diameter and ligand shell thickness play with regard to sensitivity, selectivity and speed of response to these vapors which will be reported in detail in the near furture. We believe that the MIME device will become the primary building block for a new class of miniature chemical sensing devices of the future.

ACKNOWLEDGMENT

The Office of Naval Research/Naval Research Laboratory is greatfully acknowledged for partial support of this work in the form of a sabbatical assignment to AWS.

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DEVICE SIGNAL (COUNTS)

